Available online at www.sciencedirect.com

ScienceDirect

Procedia Engineering 119 (2015) 434 – 441

Procedia Engineering

www.elsevier.com/locate/procedia

13th Computer Control for Water Industry Conference, CCWI 2015

Current perspectives on disinfectant modelling

Vanessa Speight[a]*, Joby Boxall[a]

[a]*Department of Civil and Structural Engineering, University of Sheffield, Sheffield S1 3JD UK*

Abstract

Maintenance of a disinfectant residual within water distribution systems is the final barrier in protecting public health. Hydraulic modelling software can simulate the decay of residual but application is limited by reaction and network uncertainties. The state of the art of application of disinfectant modelling is presented here in terms of reaction rate formulations and coefficients, with observations on best practice for operational simulations. Modelling disinfection behaviour assuming idealised bulk reactions, informed by site-specific point of entry tests after any blending and including temperature correction, can provide valuable insight.

Peer-review under responsibility of the Scientific Committee of CCWI 2015

Keywords: Disinfectant residual; water quality modelling; water distribution system modelling

1. Introduction

The final barrier in public health protection for many water distribution systems (WDSs) is the maintenance of a secondary disinfectant residual. This residual, typically in the form of free chlorine or chloramine, provides disinfection in case of WDS contamination, slows regrowth of microorganisms and contributes to corrosion control. Whatever disinfectant is used, it will decay during passage through the distribution system, reacting with the bulk water and with material at the pipe wall. To manage disinfectant residual, it would be ideal to have good predictions of disinfectant decay across the entire WDS. However, while hydraulic modelling of WDSs has progressed significantly since the 1990s, disinfectant modelling remains challenging and rarely effectively implemented by water utilities.

* Corresponding author. Tel.: +44(0)114 222 5750.
E-mail address: v.speight@sheffield.ac.uk

Peer-review under responsibility of the Scientific Committee of CCWI 2015
doi:10.1016/j.proeng.2015.08.906

The rate of disinfectant decay in a WDS depends on upon several factors: i) the concentration(s) of disinfectant demanding materials present in the bulk water, ii) the reaction time, iii) the temperature of the water, and iv) the concentration(s) of disinfectant demanding materials along the pipe walls during travel through the WDS coupled with the processes driving exposure to this surface. Materials with a disinfectant demand include organic matter in the treated water, corrosion products, and organic materials produced by biofilms. A variety of studies have been conducted to determine the most appropriate kinetic models incorporating these factors, with further work applying those models to real-world WDSs, which requires handling of hydraulic conditions, multiple water sources, booster chlorination, and pipe wall reactions. This paper reviews and summarises the collective experience in disinfectant modelling with a focus on practical applications and the ability to answer questions of interest in WDS operation.

2. Kinetics of Bulk Disinfectant Decay

Bulk reactions of disinfectant, either free chlorine or chloramine, have been modelled using several different kinetic formulations. A simple first-order disinfectant decay model is often used, particularly for field applications, because of the ability to determine reaction coefficients through straightforward tests [1, 2].

$$\frac{dC}{dt} = -k_b \cdot C \tag{1}$$

where C is the concentration of disinfectant (mg/L) and k_b is the bulk reaction coefficient (1/time). The reaction rate coefficient can be determined by holding a water sample at the ambient water temperature and measuring the disinfectant concentration over time. This bulk reaction test is typically performed using treated water collected from the point of entry (POE) to the WDS. Tables 1 and 2 provide a summary of first-order bulk reaction rates from previous studies for free chlorine and chloramine, respectively. The resulting reaction rate reflects the water quality at the ambient conditions and this rate, like all chemical reactions, is subject to temperature influence. The Arrhenius equation can be used to correct the bulk reaction coefficient for temperature. Chlorine decay in particular is accelerated at elevated temperatures, with an approximate doubling of reaction rates for a 5°C increase in water temperature [3]. With water temperatures ranging from 4°C to 20°C for surface waters in the UK, and even higher in warmer climates, temperature effects can lead to dramatic seasonal variations in disinfectant residual decay.

Furthermore the bulk decay rate and the initial disinfectant concentration may vary with time, as seasonal influences on raw water and daily variability in treatment flows, mixing, and dosing can alter the water chemistry. Figure 1 illustrates the variability in disinfectant concentration at the POE to the WDS for a small water treatment works in the midwestern US. Given this potential variability, it is important to account for initial conditions at the source with appropriate input data, which can be obtained from treatment works records in most cases.

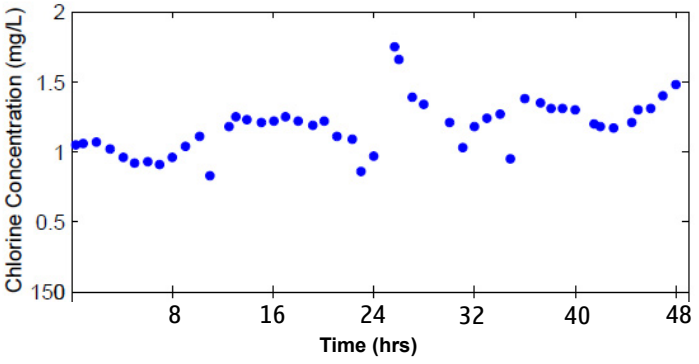

Figure 1. Example of variability in POE disinfectant concentration (adapted from [4]).

Table 1. Summary of first-order bulk decay coefficients for free chlorine

Utility	First-Order Bulk Decay Coefficient (day^{-1})	Temp. (°C)	Total Organic Carbon (mg/L)	Reference
Vercingetorix, France	0.024	14	-	[5]
Water Treatment Works A, UK	0.096	14.7	-	Unpublished results
Harrisburg, PA, USA	0.232	16.4	1.73	[1]
Cincinnati Water Works, OH, USA	0.251	22	-	[6]
Cincinnati Water Works, OH, USA	0.266	22	-	[6]
Water Treatment Plant A, Durham, NC, USA	0.372	28	-	[7]
Water Treatment Plant B, Durham, NC, USA	0.396	28	-	[7]
Eagle Reservoir Water, IN, USA	0.492	22	-	[6]
Cherry Hills/Brushy Plains Service Area, CT, USA	0.550		-	[8]
Vercingetorix, France	0.826	16	-	[6]
Bellingham, WA, USA	0.833	17.4	0.84	[1]
Fairfield, CA, USA	1.16	17.9	1.87	[1]
North Marin River Aqueduct Source, CA, USA	1.32	22.2	0.56	[1]
North Marin (Blend of Aqueduct & Lake), CA, USA	10.8	21.9	-	[1]
North Marin Lake Source, CA, USA	17.7	21.9	3.55	[1]

Table 2. Summary of first-order bulk decay coefficients for chloramine

Utility	First-Order Bulk Decay Coefficient (day^{-1})	Temp. (°C)	Total Organic Carbon (mg/L)	Reference
Water Treatment Works B, UK	0.034	16.5	-	Unpublished results
Water Treatment Plant A, Southwestern USA	0.035	16.9	-	Unpublished results
Water Treatment Plant B, Southwestern USA	0.044		-	Unpublished results
Water Treatment Plant C, Southwestern USA	0.046	16.9	-	Unpublished results
Water Treatment Plant D, Southwestern USA	0.046	19.3	-	Unpublished results
Water Treatment Works C, UK	0.046	16.4	-	Unpublished results
North Penn Keystone tie-in, PA, USA	0.082	16.2	0.79	[1]
North Penn Well W12, PA, USA	0.102	18.3	0.52	[1]
North Penn (Keystone & Forest Park blend), PA, USA	0.264	14.7	1.23	[1]
North Penn Well W17, PA, USA	0.355	14.8	1.06	[1]
North Penn Forest Park Treatment Plant, PA, USA	0.767	13.2	1.64	[1]

Natural organic matter (NOM) is the primary disinfectant demanding material in treated water and is comprised of many complex molecules, offering a variety of reaction sites and reactants. Disinfectant decay in the presence of NOM has been observed to have two phases of kinetics: fast and slow, as can be seen in Figure 2. It is

often assumed that the fast reactions take place within the treatment works at first application of disinfectant [9] when the most active and available reaction sites are used; however the truth of this assumption depends on the dosing conditions, mixing and disinfectant contact time prior to entering the WDS.

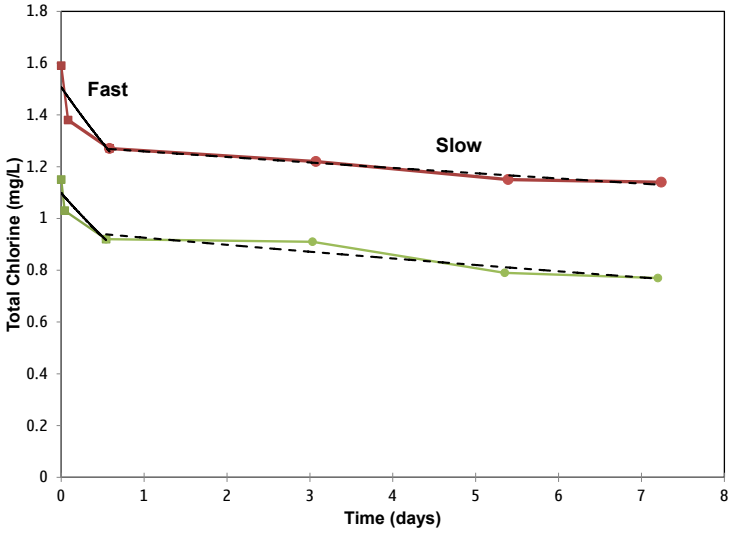

Figure 2. Example of bulk decay test results showing fast and slow chlorine reaction phases.

Several studies have shown that a second-order disinfectant decay model that incorporates a hypothetical reactant such as NOM can produce superior predictions if the concentration of disinfectant demanding material is known at different locations throughout the WDS [4,9,10,11,12]. However the measurement of NOM across a WDS and the assumption that NOM is the only reactant material limit the practicality of application of such a model formulation in the field. Attempts have been made to develop relationships between NOM and reaction rate coefficients [13] but these have not been widely used in practice. Furthermore, there are additional sources of disinfectant demanding material within the WDS, such as corrosion products and biofilm components that have been mobilised into the bulk water. A reliance on NOM as the sole reactant material may not be valid in WDSs with significant corrosion contributing to disinfectant decay at certain locations. The uncertainty associated with chlorine prediction lies primarily in network unknowns, rather than kinetic parameter uncertainty or measurement error [4].

2.1. Hydraulic Conditions

Water quality modelling is highly dependent on accurate simulation of the underlying hydraulic conditions, as these conditions form the basis for the reaction time, mixing effects and transport to and from pipe and other surfaces. Because storage facilities have such a significant impact on the time that water spends within a WDS, it is especially important to accurately represent their operation. The default assumption for storage reservoir mixing within most typical modelling packages is fully mixed, which may not be accurate for facilities experiencing stratification due to temperature effects or hydraulic short-circuiting. Furthermore, storage facilities are prone to accumulation of sediments which can contain high levels of chlorine demanding material, thereby accelerating disinfectant decay. However, the large volume to surface area of storage structures means that bulk rather than surface effects usually dominate. The mechanisms of disinfectant decay within storage facilities are largely uncharacterised and highly dependent on local conditions [14]. Modelling software such as EPANET does allow for the user to specify a different reaction rate coefficient [2] for storage facilities so field sampling could be conducted to identify reaction rates if warranted.

2.2. Multiple Water Sources

The values for first-order reaction rate coefficients given in Tables 1 and 2 illustrate the difficulty of modelling WDS with multiple sources as these sources often have different underlying water chemistries yielding different bulk reaction rates. In many cases, surface water and groundwater sources are used at different entry points to the WDS and the flow from each treatment facility can vary with customer demand, rainfall, and operational factors. The mixing of multiple sources can also occur within a storage facility partway through the WDS. Standard hydraulic modelling software packages (e.g. EPANET, commercial software) only allow for a single global bulk decay coefficient to be included [2]. Depending on the configuration of the system, the use of an average global bulk decay rate can misrepresent the chlorine kinetics so alternate strategies to correctly model the bulk rates should be used (see section 4).

2.3. Booster Chlorination

Many water utilities apply disinfectants at strategic locations within their WDS, particularly in remote areas where disinfectant residual maintenance is problematic. Booster chlorination does not have the same reaction rate coefficient as the treated water at the POE because the nature of the disinfectant demanding material has changed during travel time in the WDS to the point of booster chlorination [7,9]. Therefore new measurements of decay rate coefficients must be performed to accurately model the behaviour of booster chlorination facilities. If the decay rate coefficients following rechlorination are significantly different from the POE rate coefficients, this problem becomes the same as for multiple water sources where typical software cannot accommodate multiple bulk decay rates across a WDS. In most cases, the decay rate coefficients following rechlorination are lower than for the POE because the faster reacting material has been oxidized [9]. Therefore using the POE decay rate coefficient throughout the WDS may result in overprediction of decay following booster chlorination, which could lead to unnecessary increases in disinfectant dosing if not properly understood.

3. Pipe Wall Reactions

In addition to bulk decay, reactions with material at the pipe wall also contribute to reduction in disinfectant residual within a WDS. Most modelling software adds the effect of bulk decay to wall decay to calculate the resulting disinfectant residual concentration in a given pipe.

$$\frac{dC}{dt} = -\left(\frac{A}{V}\right) k_w \cdot C^n \tag{2}$$

where A is the surface area of pipe per unit length, V is the volume of pipe per unit length, k_w is the wall reaction rate coefficient and n is the reaction order. EPANET limits the value of n to either 0 or 1. The units of k_w are mass/area/time if n=0 and length/time if n=1. EPANET adjusts the k_w value to account for mass transfer limitations in moving reactants from the bulk to the pipe wall based on the molecular diffusivity and the Reynold's number of the flow [2]. The A/V term is important for small diameter pipes. In UK water systems where 3-inch diameter pipes are common, A/V is 1.33. In US water systems where 8-inch diameter pipes are more common, A/V is 0.5 and therefore the wall decay has a reduced effect. Zero-order kinetics for wall decay have been shown to be most appropriate for significantly corroded cast iron pipe, while first-order kinetics are a better fit for plastic pipe materials [7].

In practice, it is difficult to directly measure wall decay rates and therefore k_w becomes a calibration parameter, adjusted using global or local approaches to match field data for bulk water samples. When modelling wall decay,

an individual value for k_w can be allocated at each pipe, or pipes can be grouped by characteristics such as age or material for allocation. EPANET provides an option to estimate a wall decay rate coefficient that is proportional to the roughness coefficient [2], which can provide good results for fit to field data. Figure 3 summarizes the calibration results (84% correlation overall) for a study that included 82 chloramine grab samples collected over five days for a model with 12,000 pipes using an estimated wall decay coefficient proportional to pipe roughness.

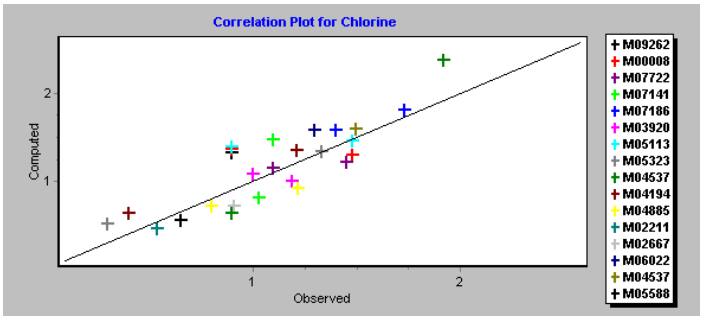

Figure 3. Calibration results for a study using estimated wall decay coefficient proportional to pipe roughness.

4. Approaches to Disinfectant Modelling

Despite the challenges in accurately modelling disinfectant behaviour, there is value in pursuing this approach to understanding WDS water quality if the appropriate uncertainties are acknowledged. Many water utilities use water age as an indicator of water quality. However, water age is surrogate, or catch all, based on the assumption that most water quality deterioration mechanisms are kinetic, it is not a measurable parameter so it is difficult to interpret and use as the basis for operational decisions. Modelling of disinfectant residual can provide a more easily understood picture of the water quality dynamics within the WDS.

One approach to modelling water quality that provides good insight into problem areas is 'ideal' disinfectant residual simulation. In this approach, a global bulk decay rate is used with no wall decay to provide a best case, or ideal, picture of disinfectant residual that would result from bulk reactions only. A comparison of the ideal simulation results with field measurements allows for identification of problem areas for further detailed investigation or intervention. An example of such an ideal disinfectant simulation is provided in Figure 4, showing model results overlain with contours derived from field sampling. In this study, large storage facilities at pump stations were found to be contributing to excess chloramine residual decay. Furthermore, the operation of these pump stations created hydraulic boundaries of stagnant water, which also contributed to disinfectant decay. For example, in Figure 4 it can be seen that the area surrounding the Acres Homes pump station is predicted to ideally have chloramine concentrations ranging from 2.5 to 3.5 mg/L (green nodes) but field data indicated low chloramine residuals below 0.5 mg/L (grey shaded area). The ideal disinfectant simulation in this case resulted in further investigation at the Acres Homes facility, including storage tank modelling, to understand and successfully correct the problems.

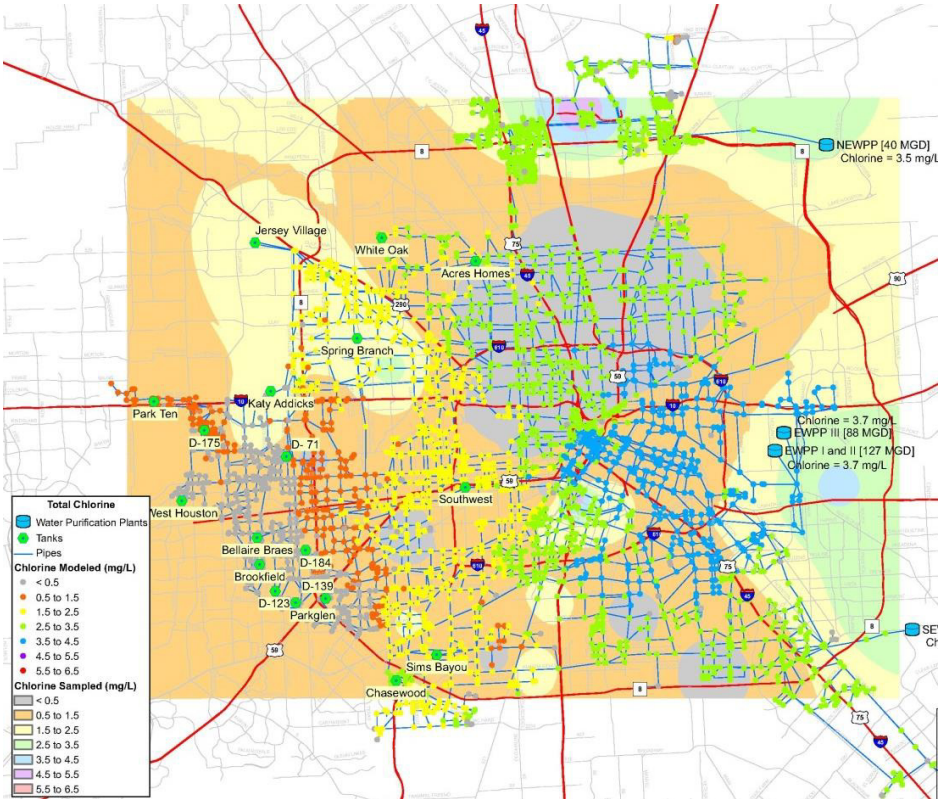

Figure 4. Example of model results for 'ideal' disinfectant residual simulation overlain with field sampling [15].

The ideal disinfectant simulation approach can also be used in the case of multiple sources of water with differing water qualities. Selecting one best case or one worst case bulk decay rate coefficient (depending on the question to be answered), simulating the ideal disinfectant concentration, and comparing the results to field samples can highlight areas with potential problems and prioritise the efforts of investigation and intervention. If warranted, a more complex modelling assessment can be performed with customised programming using the EPANET multi-species extension toolkit to incorporate several bulk decay coefficients from different POE sources to the network.

5. Conclusions

The state of the art of modelling secondary disinfection residuals within water distribution systems is typically limited by the uncertainty of reaction coefficients. The relative ease and simplicity of bulk water reaction rate tests are such that they continue to be best practice, performed on a site-specific basis at point of entry and after any blending or mixing. Software functionality is also available to account for temperature effects but is not commonly utilized; when an increase in temperature of 5°C can result in a doubling of the reaction rate this can be a critical omission.

Network modelling software often also allows for capture of the complex effects of storage within water distribution systems. While fouling can be an issue in storage structures, they have a very low surface area to volume ratio hence the bulk decay rate dominates. Hence, accuracy of modelling storage is often dependent on how well the facility and its operation comply with fully mixed conditions, if this is known and can be replicated within modelling software.

Software functionality also exists to allow for pipe wall reactions, including such effects as transport to and from the boundary layer. However, the actual reactions rates are highly pipe condition specific and hence highly uncertain. The effects of wall reactions can become dominant in systems with smaller diameter pipes, such as in the UK and Europe.

Despite the difficulties of obtaining accurate simulation results for disinfection residuals, such modelling is a powerful tool to inform systems operation and prioritise maintenance activities. Specifically, it is recommended here that running an 'ideal' bulk reaction only model, suitably informed with site specific point of entry tests, and including temperature correction, and then comparing network sample results with model predictions can readily highlight problematic regions where system improvements should be made.

Acknowledgements

The authors wish to thank the many water utilities who have provided data and funded studies. This work was funded by the UK EPSRC under the Pennine Water Group platform grant EP/I029346/1, Urban Water Systems for a Changing World.

References

[1] Vasconcelos J.J., Rossman L.A., Grayman W.M., Boulos P.F., Clark R.M. Kinetics of chlorine decay, *Journal AWWA* (1997) 89:7:54-65.
[2] Rossman, L. EPANET 2 Users Manual, EPA/600/R-00/057. 2000.
[3] Blokker M. and Speight V. Residual chlorine in the extremities of the drinking water distribution system: the influence of stochastic water demands, *Proceedia Engineering*, 70:172-180, CCWI, Perugia, Italy, 2013.
[4] Speight, V., Uber, J., Grayman, W., Martel, K., Friedman, M., Singer, P. and DiGiano, F. *Probabilistic modeling framework for assessing water quality sampling programs*, Water Research Foundation, Denver, Colorado, USA, 2009.
[5] Vasconcelos J.J., Boulos P.F. *Characterization and Modeling of Chlorine Decay in Distribution Systems*. Awwa Research Foundation, Denver, Colorado, USA, 1996.
[6] Rossman L.A., Brown R.A., Singer P.C., Nuckols J.R. DBP formation kinetics in a simulated distribution system, *Water Research* (2001) 35:14:3483-3489.
[7] DiGiano F.A., Speight V.L., Zhang W. *Disinfectant Decay and Corrosion: Laboratory and Field Studies*, Awwa Research Foundation, Denver, Colorado, USA, 2004.
[8] Rossman L.A., Clark R.M., Grayman W.M. Modeling chlorine residuals in drinking-water distribution systems, *Journal of Environmental Engineering*, ASCE, (1994) 120:4:803-820.
[9] Boccelli DL, Tryby ME, Uber JG, Summers RS. A reactive species model for chlorine decay and THM formation under rechlorination conditions, *Water Research* (2003) 37:2654-2666.
[10] Clark, R.M., Sivaganesan, M. Predicting chlorine residuals in drinking water: second order model, *J Water Res Plan Management* (2002) 128:2:152–61.
[11] Powell, J., Hallam, N., West, J., Forster, C., Simms, J., 2000. Factors which control bulk chlorine decay rates, *Water Research* 34 (1), 117-126.
[12] Fisher, I., Kastl, G. and Sathasivan, A. A suitable model of combined effects of temperature and initial condition on chlorine bulk decay in water distribution systems, *Water Research* (2012) 46:10:3293-3303.
[13] Kiene, L., Lu, W., Levi, Y. Relative importance of phenomena responsible for chlorine decay in drinking water systems. *Water Science and Technology* (1998) 38:6:219-227.
[14] Speight V, Routt J, Levine A, Besner M-C, Khanal N and Regli S. An exposure assessment methodology for water distribution storage facility contamination events, Proceedings, IWA World Water Congress and Exhibition, Montreal, Canada, 2010.
[15] Speight V.L., Li J., Kommineni S. Water quality modeling for the City of Houston, Proceedings, AWWA Water Quality Technology Conference, Denver, USA, 2006.